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U.S. Patent and Trademark Office, U.S. DEPARTMENT OF COMMERCE

**UTILITY
PATENT APPLICATION
TRANSMITTAL**

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Attorney Docket No.

AN06132US

First Inventor

Marek Gorzynski

Title

Wet STrength Agent and Method for ..

Express Mail Label No.

EL150641923US

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

1. ☒ Fee Transmittal Form (e.g., PTO/SB/17)
(Submit an original and a duplicate for fee processing)
2. ☐ Applicant claims small entity status.
See 37 CFR 1.27.
3. ☒ Specification [Total Pages 22]
(preferred arrangement set forth below)
- Descriptive title of the invention
 - Cross Reference to Related Applications
 - Statement Regarding Fed sponsored R & D
 - Reference to sequence listing, a table, or a computer program listing appendix
 - Background of the Invention
 - Brief Summary of the Invention
 - Brief Description of the Drawings (if filed)
 - Detailed Description
 - Claim(s)
 - Abstract of the Disclosure
4. ☐ Drawing(s) (35 U.S.C. 113) [Total Sheets]
5. Oath or Declaration (unsigned) [Total Pages 3]
- a. ☐ Newly executed (original or copy)
- b. ☐ Copy from a prior application (37 CFR 1.63 (d))
(for continuation/divisional with Box 18 completed)
- i. ☐ **DELETION OF INVENTOR(S)**
Signed statement attached deleting inventor(s)
named in the prior application, see 37 CFR
1.63(d)(2) and 1.63(b)
6. ☐ Application Data Sheet. See 37 CFR 1.76

ADDRESS TO:Assistant Commissioner for Patents
Box Patent Application
Washington, DC 20231

7. ☐ CD-ROM or CD-R in duplicate, large table or
Computer Program (Appendix)
8. Nucleotide and/or Amino Acid Sequence Submission
(if applicable, all necessary)
- a. ☐ Computer Readable Form (CRF)
- b. Specification Sequence Listing on:
- i. ☐ CD-ROM or CD-R (2 copies); or
- ii. ☐ paper
- c. ☐ Statements verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

9. ☐ Assignment Papers (cover sheet & document(s))
10. ☐ 37 CFR 3.73(b) Statement ☐ Power of
(when there is an assignee) Attorney
11. ☐ English Translation Document (if applicable)
12. ☐ Information Disclosure ☐ Copies of IDS
Statement (IDS)/PTO-1449 Citations
13. ☒ Preliminary Amendment
14. ☒ Return Receipt Postcard (MPEP 503)
(Should be specifically itemized)
15. ☒ Certified Copy of Priority Document(s)
(if foreign priority is claimed)
16. ☐ Request and Certification under 35 U.S.C. 122
(b)(2)(B)(i). Applicant must attach form PTO/SB/35
or its equivalent.
17. ☐ Other.

18. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment, or in an Application Data Sheet under 37 CFR 1.76:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP)

of prior application No.

Prior application information:

Examiner

Group Art Unit

For CONTINUATION OR DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 5b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

19. CORRESPONDENCE ADDRESS☐ Customer Number or Bar Code Label

(Insert Customer No. or Attach bar code label here)

or ☒ Correspondence address below

Name

Lainie E. Parker

Address

Akzo Nobel Inc.

7 Livingstone Avenue

City

Dobbs Ferry

State

NY

Zip Code

10522

Country

U.S.A.

Telephone

(914) 674-5466

Fax

(914) 693-4236

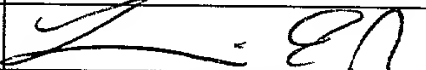
Name (Print/Type)

Lainie E. Parker

Registration No. (Attorney/Agent)

36,123

Signature



Date

11/15/00

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PTO/SB/17 (11-00)

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FEE TRANSMITTAL for FY 2001

Patent fees are subject to annual revision

TOTAL AMOUNT OF PAYMENT

(\$) 1,076.00

Complete if Known

Application Number

Filing Date

First Named Inventor

Marek Gorzynski

Examiner Name

Group Art Unit

Attorney Docket No.

AN06132US

METHOD OF PAYMENT

- 1.
- ☒
- The Commissioner is hereby authorized to charge indicated fees and credit any overpayments to

Deposit
Account
Number

01-1350

Deposit
Account
Name

Akzo Nobel Inc.

- ☒
- Charge Any Additional Fee Required
-
- Under 37 CFR 1.16 and 1.17

- ☐
- Applicant claims small entity status
-
- See 37 CFR 1.27

- 2.
- ☐
- Payment Enclosed:

- ☐
- Check
- ☐
- Credit card
- ☐
- Money
-
- Order
- ☐
- Other

FEE CALCULATION**1. BASIC FILING FEE**

Large Entity Small Entity

Fee Fee Fee Fee
Code (\$) Code (\$) Fee Description

101 710 201 355 Utility filing fee

106 320 206 160 Design filing fee

107 490 207 245 Plant filing fee

108 710 208 355 Reissue filing fee

114 150 214 75 Provisional filing fee

Fee Paid

710

SUBTOTAL (1) (\$) 710.00

2. EXTRA CLAIM FEES

Total Claims	27	-20** =	7	X	18	=	126
Independent Claims	6	-3** =	3	X	80	=	240
Multiple Dependent				X		=	

Large Entity Small Entity

Fee Fee Fee Fee
Code (\$) Code (\$) Fee Description

103 18 203 9 Claims in excess of 20

102 80 202 40 Independent claims in excess of 3

104 270 204 135 Multiple dependent claim, if not paid

109 80 209 40 ** Reissue independent claims
over original patent110 18 210 9 ** Reissue claims in excess of 20
and over original patent

SUBTOTAL (2)

(\$) 366

**or number previously paid, if greater, For Reissues, see above

FEE CALCULATION (continued)**3. ADDITIONAL FEES**

Large Entity	Small Entity	Fee Code	Fee Code	Fee Code	Fee Code	Fee Description	Fee Paid
105	130	205	65			Surcharge - late filing fee or oath	
127	50	227	25			Surcharge - late provisional filing fee or cover sheet	
139	130	139	130			Non-English specification	
147	2,520	147	2,520			For filing a request for <i>ex parte</i> reexamination	
112	920*	112	920*			Requesting publication of SIR prior to Examiner action	
113	1,840*	113	1,840*			Requesting publication of SIR after Examiner action	
115	110	215	55			Extension for reply within first month	
116	390	216	195			Extension for reply within second month	
117	890	217	445			Extension for reply within third month	
118	1,390	218	695			Extension for reply within fourth month	
128	1,890	228	945			Extension for reply within fifth month	
119	310	219	155			Notice of Appeal	
120	310	220	155			Filing a brief in support of an appeal	
121	270	221	135			Request for oral hearing	
138	1,510	138	1,510			Petition to institute a public use proceeding	
140	110	240	55			Petition to revive - unavoidable	
141	1,240	241	620			Petition to revive - unintentional	
142	1,240	242	620			Utility issue fee (or reissue)	
143	440	243	220			Design issue fee	
144	600	244	300			Plant issue fee	
122	130	122	130			Petitions to the Commissioner	
123	50	123	50			Processing fee under 37 CFR 1.17(q)	
126	180	126	180			Submission of Information Disclosure Stmt	
581	40	581	40			Recording each patent assignment per property (times number of properties)	
146	710	246	355			Filing a submission after final rejection (37 CFR § 1.129(a))	
149	710	249	355			For each additional invention to be examined (37 CFR § 1.129(b))	
179	710	279	355			Request for Continued Examination (RCE)	
169	900	169	900			Request for expedited examination of a design application	

Other fee (specify) _____

*Reduced by Basic Filing Fee Paid

SUBTOTAL (3) (\$)

SUBMITTED BY

Name (Print/Type)

Lainie E. Parker

Registration No
(Attorney/Agent)

36,123

Complete (if applicable)

Telephone (914) 674-5466

Signature

Date

11/15/00

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Patent

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	:	
M. GORZYNSKI, et al	:	
	:	Docket: ANO6132
Serial No.: Unassigned	:	
Filing Date: Even Date Herewith	:	
Priority Pat. Appln. Ser. No.: EP 99850174.6	:	Examiner:
US 60/166,564	:	
Priority Date: November 19, 1999	:	Group Art Unit:
	:	
For: WET STRENGTH AGENT AND METHOD	:	
FOR PRODUCTION THEREOF	:	

BOX PATENT APPLICATION
Assistant Commissioner of Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Sir:

Preliminary to examination, please amend the above-identified application
as follows:

IN THE SPECIFICATION:

Page 1, after the title, insert - - This application claims priority of European
Patent application No. 99850174.6, filed November 19, 1999, and U.S. Provisional
Patent Application No. 60/166,564, filed November 19, 1999.- - and
line 10, change "Background" to - -Background of the Invention- -.

Page 2, line 12, change "The Invention" to - -Summary of the Invention- -;
and

Between lines 19 and 20, insert - -Detailed Description of the Invention- -.

IN THE CLAIMS:

Please amend the following claims:

Claim 3, line 1, change "any of the claims 1-2" to - -claim 1,- -;

Line 2, after "from" insert - -the group consisting of- -; and

Line 4, change "or epoxides or" to - -epoxides and- -.

Claim 13, line 1, change "any of claims 11-12" to - -claim 11,- -;

Line 2, after "from" insert - -the group consisting of- -; and

Lines 3-4, change "or epoxides or" to - -epoxides and- -.

Claim 16, line 1, change "claims 14 or 15" to - -claim 14,- -.

Claim 17, line 1, change "claims 14-15" to - -claim 14- -.

Claim 18, line 2, after "from" insert - -the group consisting of- -; and

Line 4, change "or epoxides or" to - -epoxides,- -.

Claim 19, line 1, change "addition of" to - -adding- -.

Claim 21, line 1, change "claims 19 or 20" to - -claim 19- -.

Claim 27, line 2, change "any of claims 19-24" to - -claim 19- -.

IN THE ABSTRACT:

Line 1, change "The invention relates to a" to - -A- -.

Remarks

This preliminary amendment amends the specification, claims 3, 13, 16-19, 21 and 27, and the abstract without the addition of new matter thereby. Presently, claims 1-27 are pending.

Early and favorable consideration of this application is respectfully requested.

Respectfully submitted,



Lainie E. Parker
Attorney for Applicants
Registration No.: 36,123

Akzo Nobel Inc.
Intellectual Property Dept.
7 Livingstone Avenue
Dobbs Ferry, NY 10522-3408
(914) 674-5466

Wet strength agent and method for production thereof

The invention relates to a paper wet strength agent and a method for the
5 production of such an agent. The invention further relates to the production of paper
comprising addition of the paper wet strength agent to an aqueous cellulosic suspension
and to paper comprising a paper wet strength agent. In addition, the invention relates to
the use of a paper wet strength agent as an additive to an aqueous cellulosic suspension.

Background

10 In the papermaking art, wet strength agents like epichlorohydrin-based resins,
for example polyaminoamide epichlorohydrin resins have been used for a long time to
enhance the strength of paper. Such resins are disclosed in US 3,700,623 and US
3,772,076. The wet strength of a paper relates to its ability to maintain physical integrity
15 and to resist tearing, bursting, and shredding under use, especially under wet conditions.
A further important property of wet strengthened paper is the softness, especially for
tissue paper or the like. The softness can be described as the tactile sensation perceived
when holding or rubbing a paper across the skin.

US 5,200,036 discloses a wet strength agent which provides paper with
20 enhanced wet strength. A cationic polyaminoamide epichlorohydrin resin is modified by
introduction of a polymerisable unsaturated hydrocarbon moiety thus providing it with
ethylenically unsaturated side-chain substituents. The resin is then added to latex-forming
monomers whereby co-polymerisation occurs forming bonds between unsaturated
polymerisable hydrocarbon moieties of the resin and the latex-forming monomers. The
25 reaction may be assisted by addition of an emulsifier to obtain a desirable suspension of
the formed latex particles. Resins of the above-mentioned types are also used as
emulsifiers. Usually, the resins are not effective enough when used as a sole emulsifier
and these are thus used in combination with an additional compound.

US 5,314,721 discloses a process for preparation of vinyl polymer dispersions
30 comprising resin based on a cationic polyaminoamide whose terminal groups have been
substituted with long-chain aliphatic hydrocarbon radicals which have at least 7 carbon
atoms and are derived from monocarboxylic acids. The product obtained is used as a
sizing agent.

US 4,416,729 discloses a method for preparing wet strength additives
35 comprising the steps of contacting a linear polyamidoamine with an α,β -ethylenically
unsaturated carboxylic compound to form a substituted polyamidoamine, contacting the
substituted polyamidoamine with a polyamine to form a branched polyamidoamine

bearing a pendant amine moiety, and contacting the branched polyamidoamine with an epihalohydrin to form pendant curable ammonium moieties on the branched polyamidoamine. US 4,416,729 does not disclose use of the prepared wet strength additives for production of tissue paper.

5 Although the above epichlorohydrin-based resins in some applications show adequate wet strength and emulsifying properties, it would be desirable to be able to provide further and improved wet strength agents for paper and methods for providing such agents. It would also be desirable to be able to provide wet strength resins and agents exhibiting improved softness properties. Further, it would be desirable to be able
10 to provide further resins having improved emulsifying properties.

The Invention

 According to the present invention, it has been found that further and improved wet strength agents for paper can be obtained by a composition containing polymeric
15 particles and hydrophobic hydrocarbon groups providing side-chain substituents on wet strength resins. It has also been found a new method for the production of such wet strength resins and agents. It has further been discovered that the wet strength agents and resins produced by the method according to the present invention give paper improved softness properties without negatively affecting the absorbency properties.

20 More specifically, the invention relates to paper wet strength agents comprising polymeric particles and wet strength resins comprising a cationic nitrogen-containing polymer having hydrophobic side-chain substituents. The invention further relates to a method for the production of a paper wet strength agent comprising a first step of reacting a nitrogen-containing polymer with a hydrophobic compound to provide a nitrogen-
25 containing polymer with hydrophobic side-chain substituents, a second step of reacting the product obtained with a crosslinker to form a cationic wet strength resin, and a third step comprising emulsion polymerisation of one or more ethylenically unsaturated monomers in the presence of the wet strength resin formed. Further, the invention relates to a paper wet strength agent obtainable from the method above. The invention further
30 relates to a new wet strength resin and a method for preparing a wet strength resin according to the two first steps as described herein. The invention also relates to the production of paper comprising addition of a paper wet strength resin or agent to a cellulosic suspension and to the use of a paper wet strength resin or agent for the production of paper. The invention also relates to paper comprising paper wet strength
35 resins and agents. The invention is further defined in the appended claims.

 The present invention provides resins and agents having the ability to impart improved wet strength properties to paper. The invention further provides a simple,

convenient and effective synthetic route for the preparation of wet strength resins and agents. Thereby, the wet strength resins and agents of this invention can be prepared in high yield.

The present invention also provides wet strength resins and agents which make it possible to produce paper having enhanced softness properties. The softness of a paper sheet can be estimated by means of the relative wet strength value, which is defined as the ratio between the wet tensile index and the dry tensile index according to the formula $RWS \text{ (in \%)} = (WS/DS) \cdot 100$, where RWS stands for the relative wet strength, WS is the wet tensile index and DS is the dry tensile index of a paper. RWS is hence a measure of the softness of a paper; the higher the RWS, the higher the softness of the paper. The present wet strength resins and agents also provide improved emulsifying properties and can be used as sole emulsifiers without additional compounds which may give rise to undesirable foam formation.

The term "wet strength agent", as used herein, refers to an agent capable of imparting better wet strength properties to paper compared to paper containing no such agent. The wet strength agent comprises a wet strength resin. The term "wet strength resin", as used herein, refers to a resin capable of imparting better wet strength properties to paper compared to paper containing no such resin.

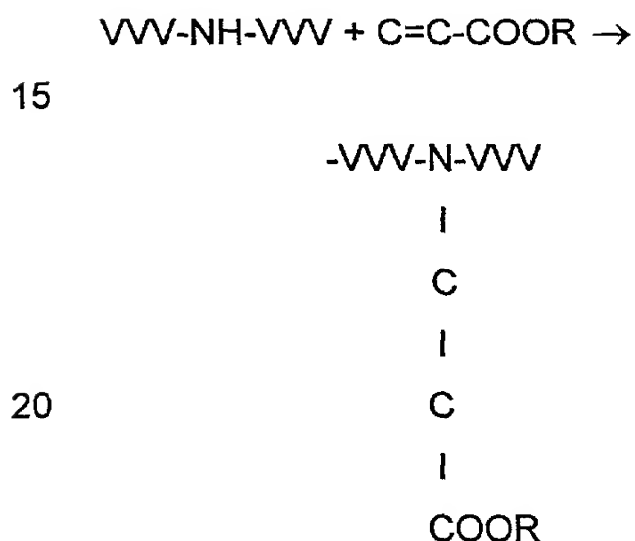
The method for the production of a paper wet strength agent comprises a first step of reacting a nitrogen-containing polymer with a hydrophobic compound to provide a nitrogen-containing polymer with hydrophobic side-chain substituents, a second step of reacting the product obtained with a crosslinker to form a wet strength resin, and a third step comprising forming of particles by emulsion polymerisation of one or more ethylenically unsaturated monomers in the presence of the wet strength resin formed. According to a preferred embodiment, no polyamine having at least 2 secondary and/or primary amine moieties, added between the first and the second step, or after the second step, is reacted.

Suitably, the nitrogen-containing polymer is a polyaminoamide, a polyamine or other nitrogen-containing polymer. Preferably, a polyaminoamide is used which may constitute the reaction product of a polycarboxylic acid, suitably a dicarboxylic acid, and a polyamine. By the term "carboxylic acid" is meant to include carboxylic derivatives such as anhydrides and esters. Suitable polycarboxylic acids include saturated or unsaturated aliphatic or aromatic dicarboxylic acids. Preferably, the polycarboxylic acids contain less than 10 carbon atoms. Suitable polycarboxylic acids include oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid and derivatives thereof. Mixtures of these compounds can also be applied. Suitable polyamines include polyalkylene polyamines, e.g. diethylenetriamine, triethylenetetramine,

tetraethylenepentamine, dipropylenetriamine and the like or mixtures thereof. Further, any polyaminoamide prepared according to a method disclosed in EP 802 215 A1, hereby incorporated by reference, may be used. Suitably, the molecular weight of the nitrogen-containing compound ranges from 100 to 50000, preferably 500 to 10000.

- 5 Suitably, the polyamine to polycarboxylic acid ratio is 0.49:1 to 1.49:1, preferably less than 1.3:1, e.g. 1.3:1 to 0.7:1. Suitably, diethylenetriamine and adipic acid are reacted to form a polyaminoamide.

Suitably, the hydrophobic compounds used can contain groups of carboxylates or derivatives thereof. The hydrophobation reaction between the nitrogen-containing
10 polymer and the hydrophobic compound can be performed via alkylation, vinylog addition or other reaction. The vinylog addition may be illustrated by the following schematic reaction:



wherein VVV-NH-VVV represents a section of the nitrogen-containing polymer,
25 $\text{C}=\text{C}-\text{COOR}$ represents a hydrophobic compound containing a vinyl group. The vinyl group, i.e. the $\text{C}=\text{C}$ group, of the hydrophobic compound can react with the nitrogen atoms of the polymer. R stands for a hydrophobic group of the hydrophobic compound which may be an alkyl, alkenyl, aryl, cycloalkyl or cycloalkenyl group. In case the vinylog reaction is applicable, the unsaturation of the vinyl group of the hydrophobic compound is
30 turned saturated after having reacted with a nitrogen atom of the polymer.

According to one preferred embodiment, the hydrophobic compound is a saturated compound, or an unsaturated compound, resulting in a nitrogen-containing polymer having saturated side-chain substituents.

The hydrophobic compounds can contain a hydrophobic group containing up to
35 40 carbons, preferably 6-40 carbons, and most preferably 8-40 carbons.

The hydrophobic chains of the hydrophobic compounds can be attached to the nitrogen-containing polymer via a chain of atoms, which can contain at least one hetero atom, via a covalent bond.

The hydrophobic compound may be selected from (meth)acrylates, alkenyl(meth)acrylate, alkyl(meth)acrylamides, esters, ethers, diazo compounds, carboxylic acids, acid anhydrides epoxides, alkyl sulphonates, alkyl sulphates and mixtures or derivatives thereof containing a hydrophobic group, preferably from alkyl(meth)acrylates, alkyl(meth)acrylamides, alkyl sulphonates, alkyl sulphates, diazo compounds, ethers, or epoxides or mixtures thereof, and most preferably from alkyl(meth)acrylates, alkyl(meth)acrylamides or mixtures thereof. Examples suitably include α, β -unsaturated esters or amides like lauryl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate, N-alkyl(meth)acrylamides, N-alkylaminoalkyl(meth)acrylamides, N,N-dialkylaminoalkyl(meth)acrylamides, N-alkylaminoalkyl(meth)acrylates, N,N-dialkylaminoalkyl(meth)acrylates, hexyl chloride, 2-ethylhexyl chloride, octyl chloride, decyl chloride, dodecyl chloride, hexadecyl chloride, octadecyl chloride, ethyl epoxide, propyl epoxide, (n-, t-, l-) butyl epoxides, pentyl epoxide, hexyl epoxide, 2-ethyl-hexyl epoxide, octyl epoxide, decyl epoxide, dodecyl epoxide, hexadecyl epoxide, octadecyl epoxide, hexene, 2-ethyl-hexene, octene, decene, dodecene, hexadecene, and octadecene.

The reaction is suitably carried out in water, neat or in other solvent, e.g. in an organic solvent, e.g. methanol, ethanol, ethylene glycol or the like, capable of at least partly dissolving the reactants without taking part in the reaction under the reaction conditions. Mixture of such solvents can also be used. The reaction is preferably carried out in water. The molar ratio nitrogen-containing polymer (based on amino mols) to hydrophobic compound can be at least 1:1, suitably 2:1 to 99:1, preferably 3:1 to 40:1. The reaction temperature may range from about 25 °C to about 150 °C, preferably from about 60 to about 90 °C.

In a second step, the hydrophobised nitrogen-containing polymers are reacted with a crosslinker. The term crosslinker or crosslinking agent, as used herein, is meant to denote a compound having the ability to crosslink the resin and/or to form bonds to cellulosic fibres. Suitably, the crosslinkers, sometimes referred to as intralinkers in EP 802 215 A1, describing various intralinkers, hereby incorporated by reference, can comprise epihalohydrins e.g. epichlorohydrin; diepoxides, diacrylates, dimethacrylates, diacrylamides, and dimethacrylamides and mixtures or derivatives thereof are used. Preferably, epichlorohydrin is used as crosslinker.

The reaction is suitably carried out in an aqueous solution, neat or by use of other solvent than water, e.g. ethanol, propanol or the like or mixtures thereof. Suitably,

the solvent can not react with the reactants under the reaction conditions used. Preferably, the reaction is carried out in water. The reaction temperature may range from about 0 °C to about 150 °C, preferably between from about 4 to about 80 °C. The molar ratio of the hydrophobised nitrogen-containing polymer (based on amino-mols) to crosslinker in the reactant composition may be 10:1 to 1:10, preferably 2:1 to 1:2.

In a third step according to the invention, the method comprises emulsion polymerisation of one or more ethylenically unsaturated monomers in the presence of the wet strength resin as formed after the second step herein. The monomers may be selected from styrene, butadiene, vinyl acetate, vinyl amide, alkyl(meth)acrylamide, alkyl(meth)acrylate, e.g. methyl (meth)acrylate, butyl (meth)acrylate, butyl glycidyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, dodecyl(meth)acrylate, octadecyl(meth)acrylate; (meth)acrylonitrile, isoprene, or 1,6-hexandiol diacrylate, or mixtures or derivatives thereof. As a result of the polymerisation process, the formed wet strength resin can be anchored to the polymeric particles formed yielding a wet strength agent. As initiator of the polymerisation reaction, any conventional initiator can be used. For example, Wako VA 044 can be used. Preferably, the initiator is water soluble. In the emulsion polymerisation reaction, the wet strength resin works as an emulsifier during the particle formation. The formed particle may be composed of one sole or a mixture of unsaturated ethylenically polymerisable monomers as above exemplified. The reaction is preferably carried out in water, organic solvents, e.g. ethanol, propanol or the like, or mixtures of organic solvents or mixtures of both water and organic solvents. The reaction temperature may range from 4 °C to about 150 °C, preferably from about 30 to about 90 °C. The weight ratio resin to monomer can be 100:1 to 1:100, suitably 10:1 to 1:50.

The invention further relates to a method for preparing a wet strength resin comprising the first and second steps of the method as above described.

The invention also relates to a wet strength agent comprising polymeric particles and a wet strength resin comprising a cationic nitrogen-containing polymer having saturated hydrophobic side-chain substituents and a derivative of a crosslinker.

The polymeric particles can be formed from polymerised monomers as described above. Preferably, monomers are selected from styrene, acrylates and mixtures or derivatives thereof.

The cationic nitrogen-containing polymer has saturated hydrophobic side-chain substituents and derivatives of a crosslinker attached to the nitrogen atoms of the polymer.

Examples of suitable nitrogen-containing polymers include well-known available commercial products which may be prepared as described above or according to

conventional methods known in the art. Examples of suitable nitrogen-containing polymers include polyaminoamides, alkyl polyamines, polyimines, and polyvinylamines.

Hydrophobic saturated side-chain substituents are attached to the nitrogen atoms of the nitrogen-containing polymer. The term hydrophobic side-chain substituent is here meant to include hydrophobic groups containing e.g. hydrophobic linear or branched hydrocarbon chains which can be linked, e.g. via a hetero atom by a covalent bond, to a nitrogen atom of the nitrogen-containing polymer. Hydrophobic groups may also include cyclic chains including cyclic hydrocarbons. Combinations of linear, branched and cyclic hydrocarbons are also included in the concept of hydrophobic groups.

The hydrophobic group of the hydrophobic side-chain can contain up to 40 carbon atoms, preferably 6-40 carbon atoms, and most preferably 8-40 carbon atoms.

The hydrophobic side-chain substituents may derive from e.g. alkyl(meth)acrylates, alkyl(meth)acrylamides, esters, ethers, diazo compounds, carboxylic acids, acid anhydrides, epoxides, alkyl sulphonates, or alkyl sulphates, or mixtures thereof containing a hydrophobic group, preferably from alkyl(meth)acrylates, alkyl(meth)acrylamides, alkyl sulphonates, alkyl sulphates, diazo compounds, ethers, or epoxides or mixtures thereof, and most preferably from alkyl(meth)acrylates, alkyl(meth)acrylamides or mixtures thereof.

Specific examples include substituents derived from α , β -unsaturated esters or amides like lauryl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate, N-alkyl(meth)acrylamides, N-alkylaminoalkyl(meth)acrylamides, N,N-dialkylaminoalkyl(meth)acrylamides, N-alkylaminoalkyl(meth)acrylates, N,N-dialkylaminoalkyl(meth)acrylates, alkyl sulphonate, alkyl sulphates, hexyl chloride, 2-ethylhexyl chloride, octyl chloride, decyl chloride, dodecyl chloride, hexadecyl chloride, octadecyl chloride, ethyl epoxide, propyl epoxide, (n-, t-, l-) butyl epoxides, pentyl epoxide, hexyl epoxide, 2-ethylhexyl epoxide, octyl epoxide, decyl epoxide, dodecyl epoxide, hexadecyl epoxide, octadecyl epoxide, hexene, 2-ethyl-hexylene, octene, decene, dodecene, hexadecene, and octadecene.

Other suitable substituents may derive from substituted succinic anhydrides containing a group selected from alkyl, alkenyl, aralkyl, or aralkenyl, and ketene dimers or multimers. Further examples of suitable substituents may be derived from the compounds disclosed in WO98/39376, hereby incorporated by reference.

A derivative of a crosslinker can be attached to the nitrogen-containing polymer which makes it possible to create bonds to nitrogen-containing polymers and/or cellulosic fibres. Derivatives of a crosslinker can be derived from epihalohydrins e.g. epichlorohydrin, diepoxides, diacrylates, dimethacrylates, diacrylamides, and

dimethacrylamides or mixtures or derivatives thereof may be used. Preferably, the crosslinker is derived from epichlorohydrin.

According to one preferred embodiment, the cationic nitrogen-containing polymer is either a polyaminoamide-epichlorohydrin resin or a polyamine-epichlorohydrin resin having saturated hydrophobic side-chains. Suitably, at least 10 % and preferably up to about 100 % of the nitrogen atoms of the cationic resin comprise cationic groups. Suitably, up to 100 % of the nitrogen atoms of the resin comprise hydrophobic groups, preferably up to 50%, most preferably 5-30 %. Suitably, the wet strength agent comprises a composition of polymeric particles and a wet strength resin dissolved in a solvent, preferably the wet strength agent comprise an aqueous composition. Suitably, the aqueous composition has a solid content of 5-50 weight percent.

The invention further relates to a wet strength resin as above described.

The invention also relates to the use of the paper wet strength resin and agent, as described above for the production of paper, preferably tissue paper. The use comprises addition of the resin or agent to an aqueous suspension containing cellulosic fibres. The amount of resin added to dry cellulosic fibres may be in any proportions, suitably 1-70, preferably 5-50, more preferably 15-50, and most preferably 25-50 kg/tonne dry cellulosic fibres. The grammage of the produced paper suitably is lower than about 70 g/m², preferably lower than about 60 g/m², and most preferably lower than 40 g/m². The paper wet strength resin and agent are preferably produced as aqueous dispersions which comprise the resin, water and optionally emulsified particles. The dispersion can then be added to an aqueous cellulosic suspension to treat paper-forming cellulosic fibres. The paper wet strength resin and agent may also be added to the produced paper and thus providing surface treatment of the paper. Further, the addition of the wet strength resin or agent may be added together with any other chemical known in the art conventionally used in the production of paper, e.g. sizing agents, softeners, retention aids, dewatering agents, dry strength agents, charge control agents or any other conventional chemicals, e.g. guar, carboxymethyl cellulose, polyacrylamide, polystyrene. Further, conventional fillers can be added thereto, e.g. clay, calcium carbonate, titanium dioxide, talc, aluminium silicate, calcium sulphate, calcium silicate or others described in WO 97/37080. Further, the wet strength agent may be added to the cellulosic fibre-containing suspension in any proportion. Before the wet strength resin or agent are added to an aqueous cellulosic suspension, the aqueous dispersion containing the resin or agent may be subjected to removal of toxic by-products by means of ion exchange, electrodialysis, enzymatical treatment, filtration, steam stripping or the like in order not to add any toxic products, e.g. chloropropandiol, dichloropropanol to the cellulosic

suspension. These methods are further described in for example EP 666 242 A1, EP 510 987 A1 and WO 92/22601.

The invention further relates to a process for the production of paper, preferably tissue paper, comprising addition of a paper wet strength resin and/or an agent as described and exemplified herein to an aqueous cellulosic suspension. The invention also relates to paper, preferably tissue paper, comprising a wet strength resin and/or an agent as described and exemplified herein. By tissue paper is generally meant items such as facial, hand, and toilet tissues used as a personal care product which comprises two key elements: a substrate formed of a planar material commonly known as tissue paper and an emollient which is carried by the substrate. In this context, tissue paper also comprises applications for domestic and industrial use, such as wiping of objects by means of kitchen rolls or the like. Tissue paper is generally produced from an aqueous suspension of cellulosic fibres, to which suspension wet strength agents have been added. The cellulose fibre-containing aqueous suspension is thereafter dewatered, suitably to a consistency of between about 7% and 25% water, suitably by means of vacuum dewatering and pressing operations such as opposing mechanical members, e.g. cylindrical rolls, to obtain a wet cellulose fibre-containing web. The dewatered web is further pressed during transfer and dried suitably by a stream drum apparatus known in the art as a Yankee dryer. Vacuum may also be applied to the web as well as multiple Yankee dryer drums, whereby additional pressing is optionally incurred between the drums, thereby forming tissue paper structures. The substrate can either consist of a single ply of tissue paper or it can comprise a laminate of two or more plies of tissue paper. In either event, since the substrate is formed of tissue paper, it is contemplated that it will be relatively thin in comparison to its dimensions in its major plane. As a relatively thin planar material, the substrate will have two major surfaces. Four important physical attributes of tissue papers are their strength, their softness, their absorbency, particularly for aqueous systems, and their lint resistance, particularly their lint resistance when wet, as further described in WO95/01478. Production methods for producing tissue paper are further described in WO95/01478, hereby incorporated by reference. More specific applications or uses of tissue paper include receiving and containing discharges from the human body, which can be used to wipe portions of the human body to remove substances therefrom, and which can be used to deposit materials thereon. The inventional paper wet strength resin or agent suitably has hydrophobic side-chains containing 6-40 carbon atoms, preferably 8-40 carbon atoms. Hydrophobic side-chains may be derived from (meth)acrylates, alkenyl(meth)acrylate, alkyl(meth)acrylamides, esters, ethers, diazo compounds, carboxylic acids, acid anhydrides, epoxides, alkyl sulphonates, alkyl sulphates and mixtures or derivatives thereof containing a hydrophobic

group, preferably from alkyl(meth)acrylates, alkyl(meth)acrylamides, alkyl sulphonates, alkyl sulphates, diazo compounds, ethers, or epoxides or mixtures thereof, and most preferably from alkyl(meth)acrylates, alkyl(meth)acrylamides or mixtures thereof. Other suitable hydrophobic side-chains may be derived from substituted succinic anhydrides containing a group selected from alkyl, alkenyl, aralkyl, or aralkenyl, and ketene dimers or multimers. Further examples of suitable hydrophobic side-chains may be derived from the hydrophobic compounds disclosed in e.g. WO98/39376, US 9,922,243, hereby incorporated by reference. The grammage of the produced tissue paper suitably is lower than about 70 g/m², preferably lower than about 60 g/m², and most preferably lower than 40 g/m². The amount of resin or agent added to a certain amount of dry cellulosic fibres may be in any proportions, suitably from about 1 to about 70 kg/tonne dry cellulosic fibres, preferably from about 5 to about 50, more preferably from about 15 to about 50, and most preferably from about 25 to about 50 kg/tonne dry cellulosic fibres. According to one preferred embodiment, a further dry strength agent is added in combination with the intentional paper wet strength resin or agent, e.g. starch, guar, carboxymethylcellulose (CMC) or a synthetic dry strength agent such as anionic or amphoteric polyacrylamides, even though the addition level of the intentional paper wet strength resin or agent to the aqueous cellulosic suspension is from about 5 to about 50 kg/tonne dry cellulosic fibres. In order to adjust a suitable dry strength of the produced tissue paper, a person skilled in the art can select a suitable hydrophobic wet strength resin or agent to obtain a desirable tissue paper, whereas the wet strength of the tissue paper can be controlled by adding an appropriate amount of resin or agent to the aqueous suspension. A tissue paper having a high relative wet strength can thereby easily be achieved.

The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the gist and scope of the present invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the claims. While the examples herebelow provide more specific details of the reactions, the following general principles may here be disclosed. The following examples will further illustrate how the described invention may be performed without limiting the scope of it.

Example 1

Reaction of a polyaminoamide (hereinafter also called PAIM) (produced from adipic acid and diethylene triamine) with a hydrophobic compound (vinyllog addition): 240 g (0.60 amino-mol equivalents) PAIM (53 % solution in water) and 27.3 g (0.15 mol) 2-

ethylhexyl acrylate (2-EHAc): were heated for 6 h and 30 min at 80 °C. Subsequently, 176 g of water was added and the solution was cooled down to room temperature. Conversion of acrylate was : 99.7 %.

307 g of the above hydrophobised PAIM solution was reacted with 30 ml epichlorohydrine (ECH) at 6 °C for 6 min. Subsequently, the temperature was increased until 20 °C was reached. The temperature was then increased until 50 °C and a viscosity of 120 mPa s was reached whereupon 155 ml of water was added and the temperature was adjusted to 65 °C to let the viscosity reach 120 mPa s. The reaction was finalised by adding 11 ml of sulfuric acid (50 %) adjusting the pH to 3.5.

Emulsion polymerisation: The ratio resin to styrene was 1:2.

A solution of 47 g of the above produced wet strength resin, 104 g water and 1.5 ml defoamer (10 % solution in water) was purged with nitrogen. The temperature was then increased to 50°C whereupon 0.5 g Wako VA 044 and 1 ml styrene were added to the solution. 10 min later, additional styrene was added (total amount: 25 g). After 5 h at 50 °C, the temperature was increased to 70 °C at which temperature the solution was kept for an hour.

Example 2

Reaction of Polyaminoamide (PAIM) with a 2-ethylhexylacrylate (2-EHAc) (vinyllog addition): 82 g (0.20 amino-mol equivalent) PAIM (52 % solution in water), 1.84 g (0.01 mol) 2-ethylhexyl acrylate (2-EHAc) and 43 g of water were heated for 2 h at 80 °C. Conversion of acrylate: 98.9 %.

15,4 ml epichlorohydrine (ECH) was added to 125 g of the above hydrophobised PAIM solution at 6 °C for 6 min. Subsequently, the temperature was increased until 20 °C was reached. The temperature was then increased to 65 °C and a viscosity of 120 mPa s was reached whereupon 86 ml of water was added. The temperature was raised to 65 °C and kept at 65 °C until the viscosity reached 120 mPa s. The reaction was finalised by addition of 11 ml sulfuric acid (50 %) adjusting the pH to 3.5.

Emulsion polymerisation: The resin/styrene ratio was 1:0.5. A solution of 88.5 g of the above wet strength resin , 92 g water and 1.5 ml defoamer (10 % solution in water) was purged with nitrogen. The temperature was increased to 45 °C. 0.04 g Wako VA 044 and 2 ml styrene were added whereafter the temperature was raised to 50 °C. After 10 minutes, additional styrene was added (total amount: 12 g). After 3 h at 50 °C, the reaction mixture was cooled down to room temperature.

Example 3

260 g (0.65 amino-mol equivalent) PAIM (53 % solution in water) (Polyaminoamide, PAIM) and 25% 41.0 g (0.16 mol) dodecyl acrylate (vinyllog addition) were heated for 4 h 30 min at 80 °C. Subsequently, 211 g water was added whereafter
5 the mixture was cooled down to room temperature.

302 g of the above hydrophobised PAIM was then reacted with 30 ml (0.20 mol) epichlorohydrine (ECH) at 6 °C for 4 min. Subsequently, the temperature was increased until 20 °C was reached. The temperature was then increased until 50 °C and a viscosity of 120 mPa s was reached. 185 ml water was then added and the temperature was
10 raised to 65 °C and kept at that temperature until the viscosity reached 120 mPa s. The reaction was finalised by addition of 10 ml sulfuric acid (50 %) adjusting the pH to 3.5.

Emulsion polymerisation: The resin/styrene ratio was 1 : 1. A solution of 75.0 g of the above wet strength resin, 100 ml water and 1 ml defoamer (10 % solution in water) was purged with nitrogen. The temperature was increased to 50°C whereupon 30 mg
15 Wako VA 044 and 1 ml styrene were added. After 10 minutes, additional styrene was added (total amount: 20.5 g). After 5 h at 50 °C, the temperature was increased to 70 °C and set at that temperature for one hour.

Example 4

20 In the emulsion polymerisation, butyl acrylate was used instead of styrene. A solution of 75.0 g of the wet strength resin of example 3 (13 % solids), and 1.5 g defoamer (10 % solution in water) was purged with nitrogen. The temperature was increased to 45°C. 0.03 g Wako VA 044 and 2 ml butyl acrylate were then added whereupon the temperature was increased to 50 °C. After ten minutes, styrene was
25 added (total amount: 14.2 ml). After 2 h 50 min at 50 °C, the temperature was increased to 70 °C which temperature was kept for one hour.

Example 5

25 % 2-ethylhexyl acrylate was used to hydrophobise PAIM. Emulsion
30 polymerisation: A solution of 121 g of the wet strength resin of example 1 (solids 28 %), 131 g water and 1 ml defoamer (10 % solution in water) was purged with nitrogen. The temperature was increased to 45°C. 0.04 g Wako VA 044 and 2 ml of a monomer mixture (styrene: 1,6-hexandiol diacrylate = 0.375 : .125) were added whereupon the temperature was raised to 50 °C in 10 min. Subsequently, the monomer mixture was added (total
35 amount: 17 g). After 3 h at 50 °C the reaction mixture was cooled down to room temperature.

Example 6

25 % 2-ethylhexyl acrylate was used to hydrophobise PAIM. A monomer mixture of styrene with t-butyl acrylate (0.45 : 0.05) was used. Emulsion polymerisation: A solution of 121 g of the wet strength resin of example 1 (solids 28 %), 131 g of water and 1 ml defoamer (10 % solution in water) was purged with nitrogen. The temperature was increased to 45°C. 0.04 g Wako VA 044 and 2 ml of a monomer mixture (styrene : t-butyl acrylate = 0.45 : 0.05) were then added and the temperature was raised to 50 °C in 10 min. Subsequently, the monomer mixture was added (total amount: 17.0 g). After 3 h at 50 °C the reaction mixture was cooled down to room temperature.

10

Example 7

630 g (1.67 amino-mol equivalent) PAIM (56 % solution in water) and 12 % (0.2 mol) dodecyl acrylate (vinyllog addition) were heated for 6 h at 80 °C. Subsequently, 326 g water was added whereafter the mixture was cooled down to room temperature. Conversion of the acrylate was: > 99 %.

15

1005 g of the above hydrophobised PAIM was then reacted with 155 g (1.68 mol) epichlorohydrine (ECH) at 6 °C for 4 min. Subsequently, the temperature was increased until 20 °C was reached. The temperature was then increased until 50 °C and a viscosity of 120 mPa s was reached. 287 ml water was then added and the temperature was raised to 65 °C and kept at that temperature until the viscosity reached 100 mPa s. The reaction was finalised by addition of 50 ml sulfuric acid (50%) and 513 ml water adjusting the pH to 3.5.

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Example 8

309.5 g (0.81 amino-mol equivalent) PAIM (55 % solution in water) and 15 % (0.12 mol) benzyl chloride (alkylation reaction) were heated for 6 h at 60 °C. Subsequently, the mixture was cooled down to room temperature.

125.5 g of the above hydrophobised PAIM was then reacted with 17.7 g (0.19 mol) epichlorohydrine (ECH) at 6 °C for 4 min. Subsequently, the temperature was increased until 20 °C was reached. The temperature was then increased until 50 °C and a viscosity of 120 mPa s was reached. 33 ml water was then added and the temperature was raised to 65 °C and kept at that temperature until the viscosity reached 100 mPa s. The reaction was finalised by addition of 6 ml sulfuric acid (50%) adjusting the pH to 3.5.

30

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Example 9

350 g (0.91 amino-mol equivalent) PAIM (55 % solution in water) and 15 % (0.14 mol) 2-ethylhexyl glycidyl ether (alkylation reaction) were heated for 7.5 h at 60 °C. Subsequently, the mixture was cooled down to room temperature.

- 5 130.4 g of the above hydrophobised PAIM was then reacted with 17.7 g (0.19 mol) epichlorohydrine (ECH) at 6 °C for 4 min. Subsequently, the temperature was increased until 20 °C was reached. The temperature was then increased until 50 °C and a viscosity of 120 mPa s was reached. 33 ml water was then added and the temperature was raised to 65 °C and kept at that temperature until the viscosity reached 100 mPa s. The reaction
10 was finalised by addition of 5.7 ml sulfuric acid (50%) adjusting the pH to 3.5.

Example 10

- 274 g (0.71 amino-mol equivalent) PAIM (55 % solution in water) and 3.8 % (0.027 mol) alkyl ketene dimer (C18-chains) were heated for 6 h at 60 °C. Subsequently, the mixture
15 was cooled down to room temperature.

- 127.2 g of the above hydrophobised PAIM was then reacted with 17.7 g (0.19 mol) epichlorohydrine (ECH) at 6 °C for 4 min. Subsequently, the temperature was increased until 20 °C was reached. The temperature was then increased until 50 °C and a viscosity of 120 mPa s was reached. 33 ml water was then added and the temperature was raised
20 to 65 °C and kept at that temperature until the viscosity reached 100 mPa s. The reaction was finalised by addition of 5.7 ml sulfuric acid (50%) adjusting the pH to 3.5.

Example 11

- 274 g (0.71 amino-mol equivalent) PAIM (55 % solution in water) and 5 % (0.036 mol) alkenyl succinic anhydride (C18-chains) were heated for 6 h at 60 °C. Subsequently, the mixture was cooled down to room temperature.

- 124.3 g of the above hydrophobised PAIM was then reacted with 17.7 g (0.19 mol) epichlorohydrine (ECH) at 6 °C for 4 min. Subsequently, the temperature was increased until 20 °C was reached. The temperature was then increased until 50 °C and a viscosity
30 of 120 mPa s was reached. 33 ml water was then added and the temperature was raised to 65 °C and kept at that temperature until the viscosity reached 100 mPa s. The reaction was finalised by addition of 5.7 ml sulfuric acid (50%) adjusting the pH to 3.5.

Example 12

185.4 g (0.48 amino-mol equivalent) PAIM (54 % solution in water) and 10 % (0.048 mol) hexanediol diacrylate (90%) were heated for 4.5 h at 80 °C. Subsequently, the mixture was cooled down to room temperature. Conversion of acrylate: > 99 %.

- 5 124.0 g of the above hydrophobised PAIM was then reacted with 17.7 g (0.19 mol) epichlorohydrine (ECH) at 6 °C for 4 min. Subsequently, the temperature was increased until 20 °C was reached. The temperature was then increased until 50 °C and a viscosity of 120 mPa s was reached. 33 ml water was then added and the temperature was raised to 65 °C and kept at that temperature until the viscosity reached 100 mPa s. The reaction
- 10 was finalised by addition of 5.7 ml sulfuric acid (50%) adjusting the pH to 3.5.

Application Testing

- Paper sheets were prepared on the dynamic sheet former "Formette". The furnish consisted of 35 % CTMP and 65 % TCF refined to 25° SR. The paper was
- 15 artificially cured 10 min at 105 °C before conditioning the paper according to DIN 5312. Tensile testing was done as described in DIN 53112. For wet tensile testing the paper was soaked 60 min at room temperature. For comparison reasons, data on paper prepared by using a conventional polyaminoamide epichlorohydrin resin has also been
- 20 given. It is to be noted that the paper sheets below appearing in tables 1-4 have been tested at three different occasions using different addition levels of the wet strength agent used. In example 1-6, 20 kg wet strength agent was added/tonne cellulosic fibres. The grammage was 55 g/m². In examples 7-12, the grammage was 30 g/m² and the addition levels of wet strength resin were 15, 20 and 30 kg/tonne cellulosic fibres. As a consequence thereof, observed values of relative strength vary between each occasion.
- 25 A reference resin, i.e. a conventional resin, has therefore been measured at each occasion as appears from the tables 1-4 below. As can be seen from the examples, the wet strength resins and agents show superior effect in view of the conventional resin used as reference at the same addition levels.

5 Table 1

Sample	Dry tensile index in Nm/g	Wet tensile index in Nm/g	Relative wet strength in %
Conventional resin	49	13	27
Example 1 Wet Strength Emulsion	37	14	37
Example 2 Wet Strength Emulsion	51	15	30
Example 3 Wet Strength Resin	37	12	32
Example 3 Wet Strength Emulsion	37	13	34
Example 4 Wet Strength Emulsion	33	12	36
Example 5 Wet Strength Emulsion	35	11	31
Example 6 Wet Strength Emulsion	37	12	33

Table 2

Sample 15 kg/ton of paper	Dry tensile index in Nm/g	Wet tensile index in Nm/g	Relative wet strength in %
Conventional resin	40,3	9,7	23,9
Example 7 Wet strength resin	31,6	9,3	29,5
Example 8 Wet strength resin	38,3	11,0	28,7
Example 9 Wet strength resin	33,6	9,0	26,7
Example 10 Wet strength resin	40,3	10,7	26,6
Example 11 Wet strength resin	35,3	10,7	30,2
Example 12 Wet strength resin	38,6	10,3	26,7

5 Table 3

Sample 20 kg/ton of paper	Dry tensile index in Nm/g	Wet tensile index in Nm/g	Relative wet strength in %
Conventional resin	41,6	10,3	24,8
Example 7 Wet strength resin	31,6	9,3	29,5
Example 8 Wet strength resin	38,0	10,8	28,5
Example 9 Wet strength resin	35,0	10,0	28,6
Example 10 Wet strength resin	39,3	11,0	28,0
Example 11 Wet strength resin	35,0	11,	31,4
Example 12 Wet strength resin	37,3	10,7	28,6

Table 4.

Sample 30 kg/ton of paper	Dry tensile index in Nm/g	Wet tensile index in Nm/g	Relative wet strength in %
Conventional resin	40,0	10,7	26,7
Example 7 Wet strength resin	31,6	10,0	31,6
Example 8 Wet strength resin	39,3	11,7	29,7
Example 9 Wet strength resin	34,0	11,0	32,4
Example 10 Wet strength resin	38,3	11,3	29,6
Example 11 Wet strength resin	34,3	11,3	33,0

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Claims

1. Method for preparing a wet strength agent comprising a first step of reacting a nitrogen-containing polymer with a hydrophobic compound to form hydrophobic side-chain substituents on the polymer, a second step of reacting the hydrophobised nitrogen-containing polymer obtained with a crosslinker to form a cationic nitrogen-containing resin, and a third step comprising forming of particles by emulsion polymerisation of one or more ethylenically unsaturated monomers in the presence of the wet strength resin formed.
2. Method according to claim 1 w h e r e i n the nitrogen-containing polymer is a polyamine or a polyaminoamide.
3. Method according to any of the claims 1-2 wherein the first step is a vinyllog addition or alkylation where the hydrophobic compound is selected from alkyl(meth)acrylates, alkyl(meth)acrylamides, alkyl sulphonates, alkyl sulphates, diazo compounds, ethers, or epoxides or mixtures thereof.
4. Method according to claim 1 w h e r e i n the hydrophobic compounds comprise a hydrophobic chain having 6-40 carbon atoms.
5. Method according to claim 1 w h e r e i n the hydrophobic compounds comprise a hydrophobic chain having 8-40 carbon atoms.
6. Method according to claim 1 w h e r e i n the hydrophobic compound contains a chain of atoms containing at least one hetero atom.
7. Method according to claim 1 w h e r e i n the crosslinker is epichlorohydrin.
8. Method according to claim 1 w h e r e i n the monomers are selected from styrene, butadiene, alkyl (meth)acrylates, alkyl(meth)amides, (meth)acrylonitrile, vinyl acetate, or vinyl amide, or mixtures or derivatives thereof.
9. Method as claimed in claim 1 w h e r e i n the hydrophobic compound is a saturated compound, or an unsaturated compound, resulting in a nitrogen-containing polymer having saturated side-chain substituents.
10. Paper wet strength agent obtainable by a method as defined in claim 9.
11. Paper wet strength agent comprising a wet strength resin comprising cationic nitrogen-containing polymers having hydrophobic saturated side-chain substituents and groups derived from a crosslinker; and polymeric particles.
12. Paper wet strength agent according to claim 11 w h e r e i n the hydrophobic side-chain substituents contain a hydrophobic group attached to a nitrogen atom of the nitrogen-containing polymer via a chain of atoms comprising 6-40 carbon atoms.
13. Paper wet strength agent according to any of claims 11-12 w h e r e i n the hydrophobic side-chain substituents are selected from derivatives of alkyl(meth)acrylates,

alkyl(meth)acrylamides, alkyl sulphonates, alkyl sulphates, diazo compounds, ethers, or epoxides or mixtures thereof.

14. Method for preparing a wet strength resin comprising a first step of reacting a nitrogen-containing polymer with a hydrophobic compound to form hydrophobic side-chain substituents, in which said hydrophobic compound is selected from alkyl(meth)acrylates, alkyl(meth)acrylamides, alkyl sulphonates, alkyl sulphates, diazo compounds, ethers, or epoxides or mixtures thereof, and a second step of reacting the hydrophobised nitrogen-containing polymer obtained with a crosslinker to form a cationic nitrogen-containing resin.

15 15. Method according to claim 14 w h e r e i n the hydrophobic compound contains 6-40 carbon atoms.

16. Method as claimed in claims 14 or 15 w h e r e i n the hydrophobic compound is a saturated compound, or an unsaturated compound, resulting in a nitrogen-containing polymer having saturated side-chain substituents.

15 17. Paper wet strength resin obtainable by a method as defined in claims 14-15.

18. Paper wet strength resin comprising cationic nitrogen-containing polymers having saturated hydrophobic side-chain substituents selected from compounds derived from alkyl(meth)acrylates, alkyl(meth)acrylamides, alkyl sulphonates, alkyl sulphates, diazo compounds, ethers, or epoxides or mixtures thereof; and groups derived from a crosslinker.

19. Process for production of tissue paper comprising addition of a paper wet strength resin or agent, comprising a cationic nitrogen-containing polymer having hydrophobic side-chain substituents, to an aqueous cellulosic suspension.

20. Process according to claim 19, wherein the paper wet strength resin or agent is added in an amount of from about 5 to about 50 kg/tonne dry cellulosic fibres.

21. Process according to claims 19 or 20, wherein the paper wet strength resin is added in an amount of from about 15 to about 50 kg/tonne dry cellulosic fibres.

22. Process according to claim 20, wherein the paper wet strength resin is added in an amount of from about 25 to about 50 kg/tonne dry cellulosic fibres.

30 23. Process according to claim 20, wherein a dry strength agent is added in combination with the paper wet strength resin or agent.

24. Process according to claim 20, wherein the produced tissue paper has a grammage lower than about 70 g/m².

25. Tissue paper comprising a paper wet strength resin or agent comprising a cationic nitrogen-containing polymer having hydrophobic side-chain substituents.

26. Tissue paper according to claim 25, wherein the tissue paper comprises a paper wet strength resin or agent in an amount from about 5 to about 50 kg/tonne dry cellulosic fibres.

27. Tissue paper comprising a paper wet strength resin or agent obtainable by a
5 method according to any of claims 19-24.

Abstract

The invention relates to a method for preparing a wet strength agent comprising a first step of reacting a nitrogen-containing polymer with a hydrophobic compound to form hydrophobic side-chain substituents on the polymer, a second step of reacting the hydrophobised nitrogen-containing polymer obtained with a crosslinker to form a cationic nitrogen-containing resin, and a third step comprising forming of particles by emulsion polymerisation of one or more ethylenically unsaturated monomers in the presence of the wet strength resin formed. The invention further relates to a wet strength agent and resin. It further relates to the use of said agent and resin in cellulosic suspensions, the production of paper, preferably tissue paper, and paper, preferably tissue paper comprising a wet strength resin or agent.

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: **WET STRENGTH AGENT AND METHOD FOR PRODUCTION THEREOF**

the specification of which:

☒ is attached hereto, and/or

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. All factual statements made in the specification of my own knowledge are true and all factual statements made on information and belief are believed to be true.

I acknowledge to the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, Sec. 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, Sec. 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Priority Claimed

<u>99850174.6</u>	<u>EUROPE</u>	<u>19 NOVEMBER 1999</u>	<u>X</u> Yes	<u> </u> No
(Number)	(Country)	(Day/Month/Year)		

I hereby claim the benefit under Title 35, United States Code § 119 of any provisional application(s) listed below:

<u>60/166,564</u>	<u>U.S.A.</u>	<u>19 NOVEMBER 1999</u>
Appln. Ser. No.	Country	Day/Month Year

I hereby claim the benefit under Title 35, United States Code, Sec. 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, Sec. 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, Sec. 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Appln. Ser. No.)	(Filing Date)	(Status: patented, pending, abandoned)
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POWER OF ATTORNEY: As a named inventor, I hereby appoint the following as my attorneys of record, with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent Office:

Louis A. Morris, Reg. No. 28,100	Richard P. Fennelly, Reg. No. 25,677
Ralph J. Mancini, Reg. No. 34,054	David H. Vickrey, Reg. No. 30,697
Lainie E. Parker, Reg. No. 36,123	Joan M. McGillicuddy, Reg. No. 35,608

Direct all correspondence to: Lainie E. Parker
Akzo Nobel Inc.
Intellectual Property Department
7 Livingstone Avenue
Dobbs Ferry, NY 10522-3408
(914) 674-5466

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Sec. 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of first inventor, if any **Marek Gorzynski**

Inventor's signature _____

Date _____

Residence Düren, Germany

Citizenship German

Post Office Address Am Courtenbachshof 3, D-52349 Düren, Germany

Full name of second joint inventor **Christian Biermann**

Inventor's signature _____

Date _____

Residence Düren, Germany

Citizenship German

Post Office Address Konenstr. 12, D-52349 Düren, Germany

Full name of third joint inventor **Heribert J. Macherey**

Inventor's signature _____

Date _____

Residence Kreuzau, Germany

Citizenship German

Post Office Address Altenweiher 15, D-52372 Kreuzau, Germany

Full name of fourth joint inventor **Arne Andersson**

Inventor's signature _____

Date _____

Residence Stenungsund, Sweden

Citizenship Swedish

Post Office Address Dagsländevägen 2, S-444 46 Stenungsund, Sweden